Studies on Nickel and Cobalt in Mineral Springs. II. Nickel and Cobalt Contents of Tentoku Mineral Spring, Saga Prefecture.

By Nobuyuki TANAKA.

(Received July 14, 1943.)

In the preceding paper[1] the colorimetric determination method for nickel and its application to some acid vitriol springs in Japan have been reported. The method was proved to be most satisfactory for the mineral springs containing a minute quantity of nickel. Of some fifteen samples that were treated by this method Wakesui in Okayama Prefecture proved the richest in nickel. However, there are some more springs in which this element is determinable. X-ray examination, for example, clearly shows them to contain a determinable amount of nickel—not only nickel but also cobalt or both of them. In these springs Tentoku in Saga Prefecture seems predominant, concerning the quantity either of nickel or of cobalt. One of the purposes of the present paper is a brief description of it and the other is to show whether or not the deposit of an ocherous ferric oxide could be accompanied by cobalt while it precipitates from mineral waters. As for nickel an experiment was carried out with a result that it was accompanied by almost no nickel, as already related in the preceding report. The same experiment was tried again in this study with the same result.

If the mineral water, especially of acid vitriol springs, is kept on standing some precipitates generally appear in it. In this regard the spring in question, Tentoku Mineral Spring, makes no exception to other springs. Therefore, the parts "filtrate" and "precipitate" were treated separately, and this treatment contributed to the investigation of the distribution of elements between these two parts.

The Filtrate Part: At first the filtrate was taken to be analysed. A spectroscopic examination by the arc method was made prior to the chemical treatment to ascertain all the main elements contained in the sample. The result is shown in Table 1. From the given result the

Table 1.

Fe, Al, Ca, Mg, Mn, Ni, Co, Si, Cu.

determinations of nickel, cobalt and the major constituents were made. Nickel was precisely determined gravimetrically by the α-benzildioxime method[2] after estimated colorimetrically by the improved Sandell's method[1]. It would go without specifying anything for the latter method, but for the former some explanations are required.

A practical application of α-benzildioxime was adovocated by F. W.

(1) N. Tanaka, this Bulletin, **18**(1943), 201.
(2) F. W. Atack, *Analyst*, **38**(1913), 318, 448.

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Atack and he claims that this reagent is very convenient for both qualitative and quantitative analyses of nickel. The fact was confirmed also by H. Grossmann *et al.* According to these investigators, nickel can be more easily separated from cobalt by this reagent than by dimethylglyoxime, which is usually employed for separating or determining the former element. The author adopted this α-benzildioxime for the determination of nickel in mineral waters, and followed the procedure described in Grossmann's report. It will be briefly mentioned.

Taking suitable volume of mineral waters, remove copper and other members of the hydrogen sulphide group by hydrogen sulphide. Expel hydrogen sulphide thoroughly and oxidize ferrous iron completely to ferric. Add the hot alcohol solution of α-benzildioxime reagent (150 c.c. of the saturated solution must be used for 0.01 g. Ni), after the sample solution was treated with ammonium citrate enough to prevent, when the solution is made ammoniacal, ferric iron from precipitating. Then make the solution slightly ammoniacal and heat it on a water-bath for a few minutes. Filter the precipitate with a glass-filter, wash it with hot 50% alcohol (more concentrated alcohol should not be used if ammonium citrate is present) and dry at 110–120°C. The temperature for the drying can be allowed up to about 180°C.

Cobalt was estimated by the nitroso-R-salt method[3], one of the colorimetric methods for cobalt. It could be only estimated, but not determined, owing to an interference considered to be caused by one or more of the elements in the given samples. As the present investigation is imperfect for the detailed discussion, it will not be gone into here. It, however, is necessary to mention that the various aliquots of the sample solution, taken to be determined colorimetrically, gave discordant cobalt contents as a result, and that the highest of these was adopted as giving the value nearest to the true one. Copper was thoroughly removed with hydrogen sulphide because it interferes with the determination. Although nickel, of course, is present in the sample, the procedure for removing it was omitted for only a reason that the nickel content is not so large compared with that of cobalt that its interference hardly requires to be taken into account. Anyway it could not be found what interferes with the cobalt determination. The matter, therefore, remains for the subsequent studies. Here will be only shown the estimated content of cobalt in Tentoku, which is remarkably large.

Table 2.

	Content (g./l.)	Content (% in total residue)
Ni	0.00927	0.0308
Co	0.00218	0.0073
Fe(Fe^{++}+Fe^{+++})	4.903	16.27
Al	0.6019	2.00
Ca	0.4306	1.43
Mg	0.8462	2.81
H_2SiO_3	0.2021	0.67
Total residue	30.143 g./l.	

The determinations of the major constituents were carried out in the usual way. Table 2 shows in the first column the contents of nickel, cobalt and major constituents in the filtrate, and in the second column the percentage of these elements in total residue.

(3) A. M. M. Davidson and R. L. Mitchell, *J. Soc. Chem. Ind.*, **59**(1940), No. 10, 232; H. T. MacPherson and J. Stewart, *Biochem. J.*, **32**(1938), 763, etc.

The Precipitate Part: The precipitate from the mineral waters was separated from the filtrate, and dissolved in concentrated hydrochloric acid. The residue was filtered, washed, ignited, and weighed as silica. The solution, on the other hand, was worked concerning the same elements as those of the filtrate. Nickel was determined only colorimetrically because of its minute quantity. The content of cobalt was obtained by the colorimetric method using nitroso-R-salt as the reagent. All results are given in Table 3, reduced to the form of oxides.

Table 3.

	Content in the precipitate from 1 l. of the water (g.)
NiO	0.0001411
CoO	0.0000138
Fe_2O_3	0.86272
Al_2O_3	0.01048
CaO	0.00772
MgO	0.00422
SiO_2	0.00159

Table 4.

	Content in the original water (g./l.)
Ni	0.00938
Co	0.00219
Fe($Fe^{++}+Fe^{+++}$)	5.506
Al	0.6075
Ca	0.4363
Mg	0.8488
H_2SiO_3	0.2042

On the Analytical Results: The data of two parts were combined to obtain the contents in the original water, which are given in Table 4. As a result it became clear that this mineral water is the richest in Japan either in nickel or in cobalt; as for the former element Wakesui, Okayama Prefecture, has predominated. Concerning the determination of the latter element in mineral springs a little has been published before this study. In our country only Kinkei Mineral Spring was the example[4]; it is estimated by the arc spectroscopic method to be less than 10 γ Co/l. and determined by the X-ray method to be 7.2 γ/l. The present investigation, however, suggested that there could be found mineral springs containing a fairly large amount of cobalt. The percentages of nickel and cobalt in total residue[5] correspond to 0.0302% and 0.0071% respectively, the former of which is far higher than the mean nickel content of acid vitriol springs in Japan. As for the latter, on the other hand, only a comparison with Kinkei is possible, showing far higher value. Moreover, the atomic ratios, Ni/Fe, Co/Fe and Co/Ni are calculated to be 16.21×10^{-4}, 3.77×10^{-4} and 0.232 respectively, as shown in Table 5. The first is also higher than the average of Ni/Fe that is represented in the last paper of this series. Co/Fe shows far and Co/Ni somewhat higher when compared with those of Kinkei.

Table 5.

	Ni/Fe	Co/Fe	Co/Ni
Atomic ratio	16.21×10^{-4}	3.77×10^{-4}	0.232

If the content of iron is assumed to be 100 the other elements analysed

(4) K. Kimura, M. Nakamura and N. Tanaka, *J. Chem. Soc. Japan*, **64**(1943), 349.

(5) 31.030 g./l. (calculated).

give the figures in Table 6. The first column is concerned with the contents in the filtrate and the second, those in the precipitate. Leaving aside the question of the major constituents, the distributions of nickel and cobalt between the filtrate and the precipitate will be taken up here. Ni/Fe in the filtrate is about ten times higher than that of the precipitate. The fact gives a full explanation to the behaviour of nickel to the ocherous ferric oxide that precipitates from mineral waters, and it proves the experience gained in the case of Kinkei to be true. The next problem is concerned with the behaviour of cobalt, which is demonstrated by the fact that Co/Fe is about twenty-five times lower in the precipitate than in the filtrate. The element, therefore, proves to remain mostly in solution, part of it migrating to the precipitate. After all, no difference can be found between nickel and cobalt regarding its remaining in solution. If there were any differences, it would be a matter of degree—the difference between the atomic ratio Co/Ni in the filtrate and that in the precipitate. The former is 0.24 and the latter 0.10. Would nickel have a somewhat closer affinity to such a deposit than cobalt? The question requires so many examples that it will be discussed in the subsequent papers.

Table 6.

	Filtrate	Precipitate
$Fe(Fe^{++}+Fe^{+++})$	100	100
Al	12.28	0.921
Ca	8.78	0.936
Mg	17.26	0.426
SiO_2	3.18	0.264
Ni	0.189	0.0184
Co	0.044_5	0.00180

Summary.

The determinations of nickel, cobalt and the major constituents in Tentoku Mineral Spring, Saga Prefecture, typical of the acid vitriol springs in Japan, have bee made. The result is that this spring contains such a remarkable amount both of nickel and cobalt that it proves to be the richest in our country in either element, showing 9.38 mg. Ni/l. and 2.19 mg. Co/l.

The distributions of these two elements between the filtrate and the precipitate have been investigated. Either of these mostly remains in the filtrate and partly migrates to the precipitate. In this regard a difference between nickel and cobalt, if it could be found, seems to be a matter of degree, that is, a problem as to which element has closer affinity to the precipitate of ferric hydroxide.

The author wishes to express his hearty thanks to Prof. Kenjiro Kimura for his kind guidance and encouragement throughout this study. The cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Department of Education, to which the author's thanks are due.

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Physico-Chemical Investigations on Catalytic Mechanism (X). On the Reaction Products in the Fischer-Tropsch Synthesis. Experimental Series II (6).

By Senzo HAMAI.

(Received August 7, 1943.)

Introduction. We have been publishing a series of papers[1] on the Fischer-Tropsch synthesis. As regards the nature of the reaction products, we have so far proceeded to determine the physico-chemical properties of the products collected in two fractions, one of which was condensed by air and water cooling and the other was condensed by the solid CO_2–C_2H_5OH mixture. Thus such properties as refractive index, specific gravity, apparent molecular weight, elementary analysis, have been obtained for these two fractions as well as the boiling point analysis by the Podbiliniak Distillation Apparatus and by a specially designed small-scale distillation apparatus, as the case may be, depending on the amount of the sample available. Some of these results have been reported in our earlier papers. Here, in this paper, we shall try to summarize some of our eariler results briefly so as to give us a more definite knowledge with regard to the nature of the reaction products as well as the relative amounts of various hydrocarbons possibly present.

Experimental Results. The results of the boiling point analysis are given for the products of the series of experiments F_{46}–F_{52}. First trap oil and second trap oil have been separately subjected to the boiling point analysis by using a specially designed small-scale distillation apparatus, and the relative amounts of possibly present hydrocarbons are graphically presented in the volume percent (Figs. 1–4). As seen in these graphs, the relative constituents in each of lighter and heavier fraction are definitely distinguishable. The lighter fraction seems to contain mainly C_6–C_9, while in the heavier fraction, predominantly C_9C_{13} are found. However, we must remember that these fractions, of course, cannot be sharply defined, but more or less they are overlapping. If the amount of a sample is sufficient, each fraction may be possibly separated and preferably subjected to more definite determinations of each physico-chemical property. At this stage we must be satisfied if we can estimate the relative magnitude of each constituent. As we have published already the data of the Podbiliniak distillation[2], correlating with these we can visualize at least what

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The most of the results given in this paper was obtained and completed in 1939–1940, but the publcation of them had been withheld.

(1) S. Hamai, S. Hayashi, K. Shimamura and H. Igarashi, this Bulletin, **17** (1942), 166–171.
S. Hamai, S. Hayashi and K. Shimamura. this Bulletin, **17**(1942), 252–259.
S. Hamai, *J. Chem. Soc. Japan*, **63**(1942), 1606–1615.
S. Hamai, S. Hayashi and K. Shimamura, this Bulletin, **17**(1942), 463–477.

(2) S. Hamai, *J. Chem. Soc. Japan*, **63**(1942), 1606–1615.

fractions usually predominate in these synthesis reactions under such conditions. Table 1 shows refractive index, apparent molecular weight, specific gravity and elementary analysis for the first trap oil and second trap oil.

The most of these results need not be discussed, for they are self-explanatory in themselves as shown respectively in the diagrams and the table. However, it should be remembered that as seen in Figs. 3 and 4, the first trap oil contains C_{12}–C_{13} predominantly as compared with C_8–C_{11} fractions, while the second trap oil contains C_7–C_9 predominantly as compared with the other fractions.

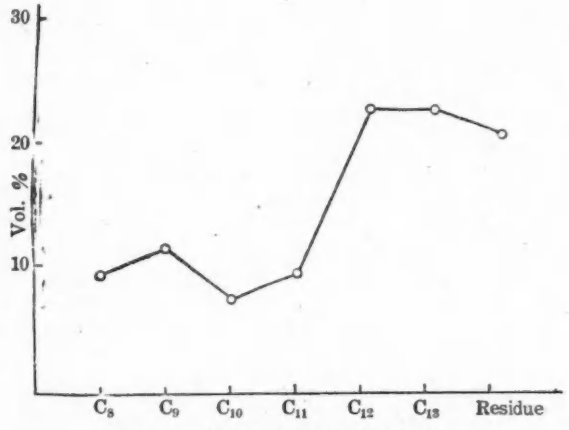

Fig. 1. Vol. % of Each Constituent.
(For 1st trap oil.)
($F_{46, 47, 49, 50, 52}$ Distillation.)

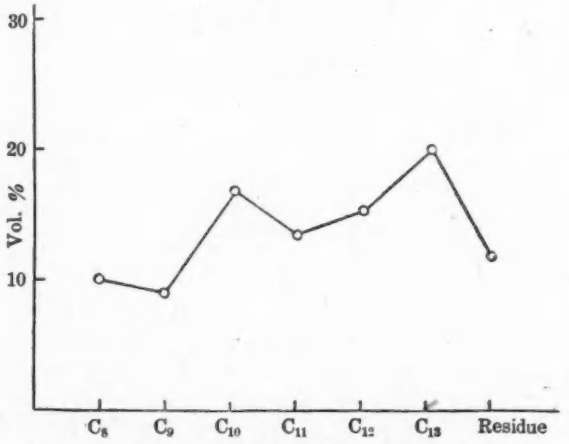

Fig. 2. Vol. % of Each Constituent.
(For 1st trap oil.)
($F_{40, 41, 42, 43, 45, 48}$ Distillation.)

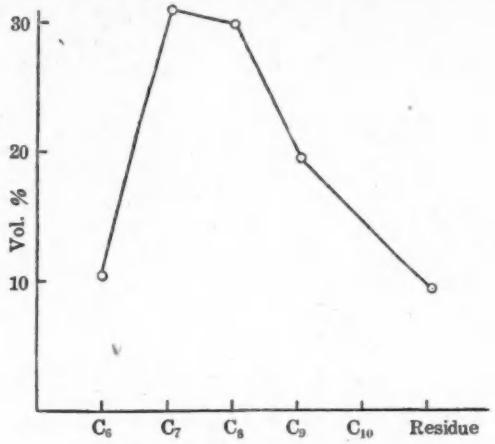

Fig. 3. Vol. % of Each Constituent.
(For 2nd trap oil.)
($F_{42,\ 43,\ 45,\ 46,\ 48,\ 50,\ 52}$ Distillation.)

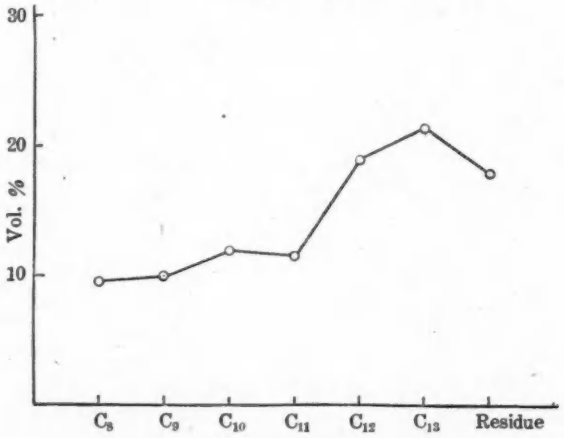

Fig. 4. Vol. % of Each Constituent.
(Fig. 1, Fig. 2, data combined.)
(For 1st trap oil.)
($F_{40,\ 41,\ 42,\ 43,\ 45,\ 46,\ 47,\ 48,\ 50,\ 52}$ Distillation.)

As regards the physico-chemical properties of these fractions of oil, the results are shown in Table 1 along with the conditions under which they are synthesized and the catalyst used. The correlations of the catalytic activity with the gas contraction and the amount of the oil yield as well as the nature of the effluent gas have already been discussed in our earlier paper[3] (VI). Also as to the effects of the promoters as boron oxide

(3) S. Hamai, this Bulletin, 17(1942), 339–344.

Table 1. Properties of the Products.

Exp. No.	React. Temp. (°C.)	Catalyst No.	Catalyst Comp. Co+CeO_2+ThO_2+B_2O_3+Cu+Kies.						Pretreatment* (hrs.)	(°C.)	Ref. Ind. 25°C. $n_D^{25°}$	Sp. Gr. 25°C. $D_4^{25°}$	App. M.W.	Elementary Analysis C (%)	H (%)
F_{40}(A-G) 1st trap oil	200	XII_{11}-1	100	15	15	–	–	100	5	400	$1.4319^{20°}$	$0.766^{20°}$	153	85.69	14.42
									5	375					
F_{40}(A-G) 2nd trap oil	200	XII_{11}-1	100	15	15	–	–	100	5	400	$1.4071^{20°}$	$0.702^{20°}$	90	85.08	15.23
									5	375					
F_{41}(A-E) 1st trap oil	190	XII_{12}-1	100	15	15	5	–	100	5	400	$1.4282^{20°}$	$0.756^{20°}$	150	84.54	15.04
									5	375					
F_{41}(A-E) 2nd trap oil	190	XII_{12}-1	100	15	15	5	–	100	5	400	$1.4050^{20°}$	$0.693^{20°}$	91	84.67	15.49
									5	375					
F_{42}( ) 1st trap oil	200	XII_{13}-1	100	18	18	5	–	100	5	400	—	—	—	—	—
									5	375					
F_{42}( ) 2nd trap oil	200	XII_{13}-1	100	18	18	5	–	100	5	400	—	—	—	—	—
									5	375					
F_{43}(A-I) 1st trap oil	200	XII_{14}-1	100	15	15	5	5	100	5	400	$1.4238^{20°}$	$0.753^{20°}$	141	84.62	15.23
									5	375					
F_{43}(A-I) 2nd trap oil	200	XII_{14}-1	100	15	15	5	5	100	5	400	$1.3863^{20°}$	$0.669^{20°}$	84	83.95	16.02
									5	375					
F_{43}(A-I) 1st trap oil	200	XII_{14}-1	100	15	15	5	5	100	5	400	1.4222	0.7507	166	84.62	15.23
									5	375					
F_{43}(A-I) 2nd trap oil I	200	XII_{14}-1	100	15	15	5	5	100	5	400	1.3924	0.6991	119	83.95	16.02
									5	375					
F_{43}(A-I) 2nd trap oil II	200	XII_{14}-1	100	15	15	5	5	100	5	400	1.3932	0.6991	119	—	—
									5	375					
F_{44}(A-D) 1st trap oil	200	XII_{15}-1	100	18	18	5	5	100	5	400	—	—	—	—	—
									5	375					

* The first line indicates the heat treatment prior to H_2 reduction and the second line shows the reduction condition by H_2.

Table 1.—(*Continued*)

Exp. No.	React. Temp. (°C.)	Catalyst No.	Catalyst Comp. Co+CeO_2+ThO_2+B_2O_3+Cu+Kies.						Pretreatment* (hrs.)	(°C.)	Ref. Ind. 25°C. $n_D^{25°}$	Sp. Gr. 25°C. $D_4^{25°}$	App. M.W.	Elementary Analysis C (%)	H (%)
F_{44}(A–D) 2nd trap oil	200	XII_{15}–1	100	18	18	5	5	100	5 5	400 375	—	—	—	—	—
F_{45}(A–H) 1st trap oil I	200	XII_{16}–1	100	15	15	10	–	100	5 5	400 375	—	0.7553	200	—	—
F_{45}(A–H) 1st trap oil II	200	XII_{16}–1	100	15	15	10	–	100	5 5	400 375	1.4259	0.7546	200	84.36	15.52
F_{45}(A–H) 1st trap oil	200	XII_{16}–1	100	15	15	10	–	100	5 5	400 375	—	0.7536	194	84.33	15.28
F_{45}(A–H) 2nd trap oil	200	XII_{16}–1	100	15	15	10	–	100	5 5	400 375	1.3966	0.6979	114	84.49	15.50
F_{46}(A–G) 1st trap oil I	200	XII_{17}–1	100	18	18	10	–	100	5 5	400 375	1.4240	0.7499	198	—	—
F_{46}(A–G) 1st trap oil II	200	XII_{17}–1	100	18	18	10	–	100	5 5	400 375	—	0.7492	204	83.73	15.40
F_{46}(A–G) 2nd trap oil	200	XII_{17}–1	100	18	18	10	–	100	5 5	400 375	—	—	—	84.42	15.52
F_{47}(A–E) 1st trap oil	200	XII_{18}–1	100	18	18	10	–	–	5 5	400 375	1.4302	0.7679	212	84.59	15.41
F_{47}(A–E) 2nd trap oil	200	X I_{18}–1	100	18	18	10	–	–	5 5	400 375	1.4107	—	131	84.77	15.61
F_{48}(A–F) 1st trap oil	200	XII_{19}–1	100	15	15	10	5	100	5 5	400 375	1.4340	0.7730	233	84.48	15.43

Table 1.—(*Concluded*)

Exp. No.	React. Temp. (°C.)	Catalyst No.	Catalyst Comp. $Co+CeO_2+ThO_2+B_2O_3+Cu+Kies.$	Pretreatment* (hrs.)	(°C.)	Ref. Ind. 25°C. $n_D^{25°}$	Sp. Gr. 25°C. $D_4^{25°}$	App. M.W.	Elementary Analysis C (%)	H (%)
F_{48}(A–F) 2nd trap oil	200	XII_{19}-1	100 15 15 10 5 100	5	400	—	—	—	84.07	15.41
				5	375					
F_{49}(A–C) 1st trap oil	200	XII_{16}-1	100 15 15 10 – 100	5	400	1.4311	—	158	—	—
				5	375					
F_{49}(A–C) 2nd trap oil	200	XII_{16}-1	100 15 15 10 – 100	5	400	1.4130	—	—	—	—
				5	375					
F_{49}(D–G) 1st trap oil	200	XII_{16}-1	100 15 15 10 – 100	5	400	1.4358	0.7707	207	84.52	15.44
				5	375					
F_{49}(D–G) 2nd trap oil	200	XII_{16}-1	100 15 15 10 – 100	5	400	1.4242	0.7316	146	85.08	15.06
				5	375					
F_{50}(A–J) 1st trap oil	200	XII_{16}-1	100 15 15 10 – 100	5	400	1.4258	0.7526	200	84.41	15.60
				5	300					
F_{50}(A–J) 2nd trap oil	200	XII_{16}-1	100 15 15 10 – 100	5	400	1.3954	0.6783	109	84.84	15.35
				5	300					
F_{51}(A–F) 1st trap oil	200	XII_{16}-1	100 15 15 10 – 100	5	400	1.4279	—	192	—	—
				5	400					
F_{51}(A–F) 2nd trap oil	200	XII_{16}-1	100 15 15 10 – 100	5	400	—	—	125	—	—
				5	400					
F_{52}(A–H) 1st trap oil	200	XII_{16}-1	100 15 15 10 – 100	5	400	1.4245	0.7508	183	84.56	15.36
				5	350					
F_{52}(A–H) 2nd trap oil	200	XII_{16}-1	100 15 15 10 – 100	5	400	1.3995	0.7014	118	84.99	15.50
				5	350					

(B_2O_3), copper as well as thorium oxide (ThO_2) and cerium oxide (CeO_2) —the effect of the pretreatment on the catalytic activity and the products etc.—, they have been collaborated in the mentioned paper. With regard to the effects of the catalyst composition on the nature and the composition of the products, we may possibly state that in main there is practically no definite conclusion[4], however, a slight variation in the properties may be found as far as these data are concerned. These facts amply justify that the distillation analysis of the products obtained by using the same series of the catalyst but differing in some of the promoters, as indicated in this paper, may be employed.

Summary.

(1) The results of the distillation analysis of the products have been graphically presented in the volume percent against each constituent and correlated.

(2) The physico-chemical properties such as refractive index, specific gravity, apparent molecular weight and the elementary analysis of the products along with experimental conditions and the catalyst used have been tabulated.

(3) As regards the effects of the catalyst composition on the nature and the composition of the products, we may posibly state that there is practically no definite conclusion, however, a slight variation may be found, as far as these series of data and the catalyst are concerned.

In conclusion, the author expresses his hearty thanks to Dr. T. Marusawa, Former Director, and to Dr. S. Sato, Director of the Institute, for their interests and constant encouragement in carrying out this series of investigations and for the permission for this publication. Also the author takes this occasion to extend his thanks to Messrs. Hayashi, Shimamura, Fujiwara, Igarashi and Kuwabara, who have been willing to assist him in the experimental part of this investigation and to Messrs. Kataoka, Inaba, Kodama and Nakano who have helped him in the part of the analytic work.

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(4) It is rather difficult to estimate, from these physico-chemical properties, whether these fractions contain normal or isomeric forms, but as we have already mentioned that Boron Oxide (B_2O_3) or Cerium Oxide (CeO_2) play a very important role as an "Electron Carrier" or "Oxygen Carrier" enabling us to explain a possible existence of isomeric forms detected by the Podbiliniak analysis. See also reference (2) and Egloff, "Physical Constants of Hydrocarbons," Vol. I.

Hydrocarbon Conversion with Special Reference to the Thermodynamical Calculations for the Isomerization Reactions. I.

By Senzo HAMAI.

(Received July 15, 1943.)

Synopsis. (1) In order to grasp the general trend of isomerization reactions of saturated hydrocarbons, the free energy equations, as a function of temperature convenient for practical calculations, are derived based on one of the more recent data available.

(2) Making use of these derived simple free energy equations, ΔF's at 0°, 25°, 100°, 200° and 300°C. are computed and tabulated and compared with those of other sources.

(3) The free energy equations of some of the useful reactions such as the formation of neohexane by alkylation, and the formation of isooctane by the coupling reaction of isobutene and isobutane are derived and ΔF's are calculated.

(4) Discussions in connection with these thermodynamical calculations for isomerization reactions are presented.

(5) Discussions of the isomerization in connection with so-called "Bond Free Energy Equation" of Bruins and Czarnecki are presented.

(6) In general, isomerization reactions of hydrocarbons, with few exceptions, are favoured thermodynamically at a lower temperature.

(7) Isomerization reactions from simpler structures to more complicated and branched compounds are favoured thermodynamically, more or less, at a lower temperature.

(8) In the isomerization reactions of di- or tri-methylated compounds involving merely an exchange of the position of the carbon to which methyl or ethyl groups are attached, a structure which is more non-symmetrical favours the isomerization thermodynamically at a higher temperature.

(9) Free energy changes involved in the isomerization reactions are of small magnitude as compared with those of ordinary chemical reactions.

(10) The errors involved in the data of the free energy changes of isomerization often amount to a magnitude as big as the free energy change itself. Hence in the selection of data for such calculations, much caution should be taken into consideration.

Introduction. In connection with the investigations of hydrocarbon chemistry, especially in the field of hydrocarbon synthesis, one of the most vital problems is, of course, to obtain justly the desired products without much interference as caused by the various possible side reactions which usually occur almost in any type of synthesis without exception, possibly. However, such a pure reaction is very much desirable and it may be possible in the laboratory scale, but if such a process is industrialized, on account of the necessity of increasing the yield, the pureness of the process is usually sacrificed. Consequently, we are confronted with the situation in which the undesired products must be converted to the desired ones. Such situations are very obviously the case in the liquid fuel synthesis where very many kinds of products are formed, whether desired or not, so that we are naturally forced to separate them and furthermore to proceed with the task of conversion of hydrocarbons, such as normal hydrocarbons changed into the respective isomers.

The isomerization[1] reaction of hydrocarbons, along with cyclization, alkylation, polymerization etc. are very important in improving the quality of liquid fuel. These have long been investigated by various investigators, and their contributions are enormous, above all in the studies on polymer gasoline, the cyclization of heptance to obtain toluene, and the cyclization of octane to xylene, etc., as well as the isomerization of butane, and other normal paraffins, and also the formation of neohexane by alkylation of isobutane in the presence of ethylene, and so on.

The purpose of this paper is to show the thermodynamical possibility of such isomerizations for saturated hydrocarbons (I) and for unsaturates (II)[2] in a systematic way. The free energy changes for isomerization reactions[1] often involve errors as many as the free energy change itself. Therefore, in order to get a reasonable estimation of the free energy change by means of the combination of the free energy data from various sources, the data must be very carefully selected. For such precaution, we have consistently based our calculation on one of the most recent investigations[3] of which the data seem to have been very consistently selected, although the absolute magnitude may differ from those of other sources. This attitude of calculation is amply justified for this kind of calculation, for the relative magnitude of changes are only important.

Derivations of Free Energy Equations. One of the fundamental equations for the standard free energy of formation as a function of temperature is obviously shown by

$$\Delta F = \Delta H - T\Delta S \qquad (1)$$

where ΔF, ΔH, T and ΔS stand for the usual significance—the same notations as used by Lewis and Randall[4].

As seen in the equation, the free energy of any type of reaction can easily be obtained if the heat of reaction ΔH and the entropy of all substances involved are given at that temperature. The free energy and the heat of formation at any given temperature are connected as:

$$\frac{d(\Delta F/T)}{dT} = -\Delta H/T^2 . \qquad (2)$$

From the above-cited relation, the free energy equation may be obtained as a function of temperature, but of course, in order to get the relation usable in practical calculation we must use such a relation as:

$$\left(\frac{\partial \Delta H}{\partial T}\right)_p = \Delta C_p , \qquad (3)$$

(1) E. Wilson, *Chem. Rev.*, **21**(1937), 129–167; C. D. Nenitzescu, *angew. Chem.*, **52**(1939), 232; H. Shingu, *J. Ind. Chem. Japan*, **46**(1943), 175.

(2) (II) To be published in part II of this series of papers on unsaturated hydrocarbons.

(3) C. M. Thacker, H. O. F. Folkins and E. L. Miller, *Ind. Eng. Chem.*, **33** (1941), 584–590.

(4) Lewis and Randall, "Thermodynamics," 1923.

which is known as Kirchhoff's formula. Using (4) in (3) we obtain (5),

$$\left.\begin{aligned} C_p &= \Gamma_0+\Gamma_1 T+\Gamma_2 T^2+\Gamma_3 T^3+\cdots\cdots\cdots \\ \Delta C_p &= \Delta\Gamma_0+\Delta\Gamma_1 T+\Delta\Gamma_2 T^2+\cdots\cdots\cdots\cdots \end{aligned}\right\} \qquad (4)$$

$$\Delta H = \Delta H_0+\Gamma_0 T+1/2\,\Gamma_1 T^2+1/3\,\Gamma_2 T^3+\cdots\cdots \qquad (5)$$

Then substituting it in (2) and by integration of such relation, the desired relation of the free energy as a function of temperature may possibly be obtained, namely:

$$\Delta F^\circ = \Delta H_0-\Gamma_0 T\ln T-1/2\,\Gamma_1 T^2-1/6\,\Gamma_2 T^3+\cdots\cdots+IT\,. \qquad (6)$$

Using these relationships, Thacker, Folkins and Miller[2] have recently published the free energy equations of formation for some seventy-seven hydrocarbons and others. The present author, with the aid of the mentioned literature, along with various other published data[5] as of Thomas, Egloff and Morrell, Rossini and Pitzer, has derived simple free energy equation for the isomerization reactions and computed the free energy changes at 0°, 25°, 100°, 200° and 300°C.

The free energy equations were derived in the form of:

$$\Delta F^\circ = A+BT\,, \qquad (7)$$

where A's and B's are constants.

From such a simple relationship for ΔF° as a function of temperature, we may grasp very easily the change of free energy at any temperature, i.e., the thermodynamical possibility of various isomerization reactions important in the field of industrial synthesis. Table 1 gives these free energy equations as well as ΔF's at various temperatures. Table 2 shows the comparison of ΔF's at 298.16°K. between our calculations and those of other sources available. Table 3 compiles the ΔF°'s for various important hydrocarbons in order to show how they differ from those data compiled and selected by different authors, for the sake of thoroughness.

Discussions. In examining the tables, we find that the reactions as written are seen very definitely to be more favourable if the temperature is lower i.e., the lower the temperature, the more favourable the reaction from the left to right is, except for a few as Nos. 11, 16, 17, 19, 35, 47, which are easily seen in the table. In the reaction, *n*-butane=isobutane, at 200°C., ΔF° is found to be positive, while in the case of *n*-pentane=isopentane, even at 300°C., ΔF° is still negative. In the case of *n*-pentane=tetramethylmethane even at 200°C., ΔF° is already a

(5) (a) Thomas, Egloff and Morrell, *Ind. Eng. Chem.*, **29**(1937), 1260.
(b) F. D. Rossini, *Chem. Rev.*, **27**(1940), 1–15.
(c) K. S. Pitzer, *Chem. Rev.*, **27**(19140), 39–57.

positive quantity. The formation of neohexane shows positive $\Delta F°$ at 200°C., while by alkylation of isobutane to get neo-hexane it is found to be thermodynamically very much favourable. As regards the transformation between dimethylated compounds, as 2,2-dimethylbutane=2,3-dimethylbutane, $\Delta F°$ favours the reaction if carried over at a higher temperature. The same is true in the case of

$$\left.\begin{matrix}\text{2,2-dimethylpentane}\\ \text{3,3-dimethylpentane}\end{matrix}\right\} = \left\{\begin{matrix}\text{2,3-dimethylpentane}\\ \text{2,4-dimethylpentane}\end{matrix}\right.$$

$$\left.\begin{matrix}\text{2,2-dimethylpentane}\\ \text{3,3-dimethylpentane}\end{matrix}\right\} = \left\{\begin{matrix}\text{2-methylhexane}\\ \text{3-methylhexane}\\ \text{3-ethylpentane}\end{matrix}\right.$$

and few others already mentioned. In the case of tri- or tetra-methylated compounds, the decreasing of $\Delta F°$'s was found to be more or less at a lower temperature. *n*-heptane and methylated heptane or *n*-octane seem to be very easily transformed to more complicated and branched compounds over wide ranges of temperature as illustrated in 2-methylheptane, 3-methylheptane and 4-methylheptane, respectively, going over to 2,2,3,3-tetramethylbutane, as well as *n*-heptane into 2-methylhexane, 3-methylhexane and 3-ethylpentane etc. These facts seem very reasonable as compared with the fact that *n*-heptane, in the presence of chromium oxide gel catalyst, easily is converted to toluene, by the cyclization process[6].

P. F. Bruins and J. D. Czarnecki[7] recently published a very interesting paper in connection with the relation between structure and free energy of organic molecules and proposed empirically, so-called "Bond Free Energy Equation". The idea of this bond free energy equation is very suggestive as well as very practicable and convenient to some extent in the calculation of free energy for the reactions in the engineering purpose. As they called attention to the relation between structure and free energy values, some possible and useful correlation may be obtained if the structure of these hydrocarbons and bond free energy are considered; for instance such reaction as isopentane=tetramethylmethane (neopentane), of which the skeleton structure can be represented as:

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(6) S. G. Goldwasser and H. S. Taylor, *J. Am. Chem. Soc.*, **61**(1939), 1766–1769; S. Kinumaki, N. Kawatake and Asakura, "Nippon Gakujutsu Kyokai," Report No. 16 (1941), 52–54; D. J. Salley, H. Fehrer and H. S. Taylor, *J. Am. Chem. Soc.* **63**(1941), 1131–1133; J. D. Turkevich, H. Fehrer and H. S. Taylor, *J. Am. Chem. Soc.*, **63**(1941), 1129–1131; H. S. Taylor and J. Turkevich, *Trans. Faraday Soc.*, **35** (1939), 921.

(7) P. F. Bruins and J. D. Czarnecki, *Ind. Eng. Chem.*, **33**(1941), 201–203.

(8) ($C–CH_3$) type bond, according to Bruins and Czarnecki, was introduced instead of finding the correction factors for C–C, and C–H type bonds as influenced by various substitutions.

$$\begin{array}{c} \text{C–C–C–C} \\ \quad\;\; | \\ \quad\;\; \text{C} \end{array} \rightleftarrows \begin{array}{c} \quad\;\; \text{C} \\ \quad\;\; | \\ \text{C–C–C} \\ \quad\;\; | \\ \quad\;\; \text{C} \end{array},$$

where in isopentane, $3(C\text{–}CH_3)$[8], $1(C\text{–}C)$, $12(C\text{–}H)$ bonds and in tetramethylmethane, $4(C\text{–}CH_3)$, $12(C\text{–}H)$ bonds are involved. Therefore from the concept of Bond Free Energy Equation, $\Delta F°$ for isomerization can be represented roughly as:

$$\Delta F_{3(C\text{–}CH_3)} + \Delta F_{1(C\text{–}C)} + \Delta F_{12(C\text{–}H)} + \delta F_i^\circ = \Delta F_{4(C\text{–}CH_3)} + \Delta F_{12(C\text{–}H)}.$$

Therefore,
$$\delta F_i^\circ = \Delta F_{1(C\text{–}CH_3)} - \Delta F_{1(C\text{–}C)} \qquad (8)$$

but more elaborately speaking, it should be

$$\delta F_i^{\circ\prime} = \Delta F_{1(C\text{–}CH_3)} - \Delta F_{1(C\text{–}C)} + \Delta F_{3(C\text{–}H)}' - \Delta F_{2(C\text{–}H)}'' - \Delta F_{1(C\text{–}H)}'''. \qquad (9)$$

This can be seen from the comparision of the data from (8) and $\Delta F° = -2739 + 7.1T$ respectively, -13166 cal. and -623 cal. (Considerable difference). Therefore the difference in these values is probably due to the fact that the term[9] $(3(H\text{–}H)^{I} - 2(C\text{–}H)^{II} - (C\text{–}H)^{III})$ is neglected, in other words, using these bond free energy equations, differentiation between $(C\text{–}H)^{I}$, $(C\text{–}H)^{II}$ and $(C\text{–}H)^{III}$ should be borne in mind. Otherwise, the agreement between such calculations cannot be expected. This does not mean that the idea of Bond Free Energy Equation is useless, but it only shows that Bond Free Energy Equation must be so refined for different types of bonds as modified and influenced by various substitutions of the groups. At any rate, such calculation carried out in Bond Free Energy Equation, may be useful at least for the engineering purpose, as the types of calculations illustrated in Bruins and Czarnecki's publication.

As observed in the values of $\Delta F°$'s at various temperatures, the free energy changes involved in the isomerization reactions are of small magnitude, and as already stated, the errors involved are sometimes as big as the $\Delta F°$ itself[10]. Therefore, before we get any definite conclusion, more refined and accurate data must be obtained. Though the present situation may not give a precise conclusion, the general trend of, and aspects of isomerization reaction with a special reference to their thermodynamical possibility may be grasped; at least, the relative changes in the possibility of transformation with respect to the variation of temperature, which is one of the most important factors, may be ascertained.

The free energy equations for some of the useful reactions such as the formation of neohexane from the alkylation of isobutane, and the formation of 2,2,4-trimethylpentane (isooctane) from the coupling of isobutene and isobutane are also derived and $\Delta F°$'s for these reactions also are shown.

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(9) Probably other factors also may be responsible for these discrepancies (such as (C–C) bond etc.).

(10) E. Wilson, *Chem. Rev.*, **21** (1937), 129–167.

Table 1. Equations for Free Energies of Isomerization Reactions as a Function of Temperature.

	Reactions	Free Energy Equations $\Delta F^\circ = A + BT$		ΔF° cal./mol.				
		A	*B*	0°	25°	100°	200°	300°
1	*n*-Butane = Isobutane	− 1635	+ 4.0	− 543	− 443	− 143	+ 257	+ 657
2	*n*-Pentane = Isopentane	− 1932	+ 2.8	− 1167	− 1097	− 887	− 607	− 327
3	*n*-Pentane = Tetramethylmethane	− 4671	+ 9.9	− 1967	− 1720	− 977	+ 13	+ 1003
4	Isopentane = Tetramethylmethane	− 2739	+ 7.1	− 800	− 623	− 90	+ 620	+ 1330
5	*n*-Hexane = 2,2-Dimethylbutane (Neohexane)	− 4650	+11.1	− 1619	− 1341	− 509	+ 601	+ 1711
6	Isobutane + C_2H_4 = 2,2-Dimethylbutane (Neohexane) $\Delta F^\circ = -25178 + 2.303 \times 2.72T \log T - 19.55 \times 10^{-2}T^2 + 12.94T$			−18934	−18437	−17060	−15505	−14281
7	*n*-Hexane = 2,3-Dimethylbutane	− 3550	+ 8.0	− 1365	− 1165	− 565	+ 235	+ 1035
8	*n*-Hexane = 2-Methylpentane / 3-Methylpentane	— 1750	+ 4.0	− 658	− 558	− 258	+ 142	+ 542
9	2-Methylpentane / 3-Methylpentane = 2,2-Dimethylbutane	− 2900	+ 7.1	− 961	− 783	− 251	+ 459	+ 1169
10	2-Methylpentane / 3-Methylpentane = 2,3-Dimethylbutane	− 1800	+ 4.0	− 708	− 608	− 308	+ 92	+ 492
11	2,2-Dimethylbutane = 2,3-Dimethylbutane	+ 1100	− 3.1	+ 253	+ 176	− 57	− 367	− 677
12	*n*-Heptane = 2,2-Dimethylpentane / 3,3-Dimethylpentane	− 4710	+ 9.7	− 2061	− 1818	− 1091	− 121	+ 849
13	*n*-Heptane = 2,3-Dimethylpentane / 2,4-Dimethylpentane	− 3610	+ 6.6	− 1808	− 1643	− 1148	− 488	+ 172
14	*n*-Heptane = 2-Methylhexane / 3-Methylhexane / 3-Ethylpentane	− 1810	+ 2.6	− 1100	− 1035	− 840	− 580	− 320
15	*n*-Heptane = 2,2,3-Trimethylbutane	− 6510	+13.7	− 2769	− 2426	− 1399	− 29	+ 1341
16	2,2-Dimethylpentane / 3,3-Dimethylpentane = 2,3-Dimethylpentane / 2,4-Dimethylpentane	+ 1100	− 3.1	+ 253	+ 176	− 57	− 367	− 677
17	2,2-Dimethylpentane / 3,3-Dimethylpentane = 2-Methylhexane / 3-Methylhexane / 3-Ethylpentane	+ 2900	− 7.1	+ 961	+ 783	+ 251	− 459	− 1169
18	2,2-Dimethylpentane / 3,3-Dimethylpentane = 2,2,3-Trimethylbutane	− 1800	+ 4.0	− 708	− 608	− 308	+ 92	+ 492

Table 1.—(*Continued*)

	Reactions	Free Energy Equations $\Delta F° = A + BT$		$\Delta F°$ cal./mol.				
		A	*B*	0°	25°	100°	200°	300°
19	2,3-Dimethylpentane + 2,4-Dimethylpentane = 2-Methylhexane + 3-Methylhexane + 3-Ethylpentane	+ 1800	− 4.0	+ 708	+ 608	+ 308	− 92	− 492
20	2,3-Dimethylpentane + 2,4-Dimethylpentane = 2,2,3-Trimethylbutane	− 2900	+ 7.1	− 961	− 783	− 251	+ 459	+ 1169
21	3-Methylhexane + 2-Methylhexane + 3-Ethylpentane = 2,2,3-Trimethylbutane	− 4700	+11.1	− 1669	− 1391	− 559	+ 551	+ 1661
22	*n*-Octane = 2-Methylheptane + 3-Methylheptane + 4-Methylheptane + 3-Ethylhexane	− 1770	+ 4.0	− 678	− 578	− 278	+ 122	+ 522
23	*n*-Octane = 3-Methyl-3-ethylpentane + 2,2-Dimethylhexane + 3,3-Dimethylhexane	− 4670	+11.1	− 1639	− 1361	− 529	+ 581	+ 1691
24	*n*-Octane = 2-Methyl-3-ethylpentane + 2,3-Dimethylhexane + 2,4-Dimethylhexane + 2,5-Dimethylhexane + 3,4-Dimethylhexane	− 3570	+ 8.0	− 1385	− 1185	− 585	+ 215	+ 1015
25	*n*-Octane = 2,3,4-Trimethylpentane	− 5470	+12.0	− 2193	− 1893	− 993	+ 207	+ 1407
26	*n*-Octane = 2,2,3-Trimethylpentane + 2,3,3-Trimethylpentane	− 6470	+15.1	− 2346	− 1969	− 836	+ 674	+ 2184
27	*n*-Octane = 2,2,4-Trimethylpentane	− 6470	+12.8	− 2974	− 2654	− 1694	− 414	+ 866
28	*n*-Octane = 2,2,3,3,-Tetramethylbutane	− 9370	+22.2	− 3307	− 2752	− 1087	+ 1133	+ 3353
29	2-Methylheptane + 3-Methylheptane + 4-Methylheptane + 3-Ethylhexane = 3-Methyl-3-ethylpentane + 2,2-Dimethylhexane + 3,3-Dimethylhexane	− 2900	+ 7.1	− 961	− 783	− 251	+ 459	+ 1169

Table 1.—(*Continued*)

	Reactions	Free Energy Equations $\Delta F° = A + BT$		$\Delta F°$ cal./mol.				
		A	*B*	0°	25°	100°	200°	300°
30	2-Methylheptane 3-Methylheptane 4-Methylheptane 3-Ethylhexane = 2-Methyl-3-ethylpentane 2,3-Dimethylhexane 2,4-Dimethylhexane 2,5-Dimethylhexane 3,4-Dimethylhexane	− 1800	+ 4.0	− 708	− 608	− 308	+ 92	+ 492
31	2-Methylheptane 3-Methylheptane 4-Methylheptane 3-Ethylhexane = 2,3,4-Trimethylpentane	− 3600	+ 8.0	− 1415	− 1215	− 615	+ 185	+ 985
32	2-Methylheptane 3-Methylheptane 4-Methylheptane 3-Ethylhexane = 2,2,3-Trimethylpentane 2,3,3-Trimethylpentane	− 4700	+11.1	− 1669	− 1391	− 559	+ 551	+ 1661
33	2-Methylheptane 3-Methylheptane 4-Methylheptane 3-Ethylhexane = 2,2,4-Trimethylpentane	− 4700	+ 8.8	− 2297	− 2077	− 1417	− 537	+ 343
34	2-Methylheptane 3-Methylheptane 4-Methylheptane 3-Ethylhexane = 2,2,3,3-Tetramethylbutane	− 7600	+18.2	− 2630	− 2175	− 810	+ 1010	+ 2830
35	3-Methyl-3-ethylpentane 2,2-Dimethylhexane 3,3-Dimethylhexane = 2-Methyl-3-ethylpentane 2,3-Dimethylhexane 2,4-Dimethylhexane 2,5-Dimethylhexane 3,4-Dimethylhexane	+ 1100	− 3.1	+ 253	+ 176	− 57	− 367	− 677

Table 1.—(*Continued*)

	Reactions	Free Energy Equations $\Delta F^\circ = A + BT$		ΔF° cal./mol.				
		A	*B*	0°	25°	100°	200°	300°
36	3-Methyl-3-ethylpentane 2,2-Dimethylhexane 3,3-Dimethylhexane =2,3,4-Trimethylpentane	− 700	+ 0.9	− 454	− 432	− 364	− 274	− 184
37	3-Methyl-3-ethylpentane 2,2-Dimethylhexane 3,3-Dimethylhexane =2,2,3-Trimethylpentane + 2,3,3-Trimethylpentane	− 1800	+ 4.0	− 708	− 608	− 308	+ 92	+ 492
38	3-Methyl-3-ethylpentane 2,2-Dimethylhexane 3,3-Dimethylhexane =2,2,4-Trimethylpentane	− 1800	+ 1.7	− 1336	− 1293	− 1166	− 996	− 826
39	3-Methyl-3-ethylpentane 2,2-Dimethylhexane 3,3-Dimethylhexane =2,2,3,3,-Tetramethylbutane	− 4700	+11.1	− 1669	− 1391	− 559	+ 551	+ 1661
40	2-Methyl-3-ethylpentane 2,3-Dimethylhexane 2,4-Dimethylhexane 2,5-Dimethylhexane 3,4-Dimethylhexane =2,3,4-Trimethylpentane	− 1800	+ 4.0	− 708	− 608	− 308	+ 92	+ 492
41	2-Methyl-3-ethylpentane 2,3-Dimethylhexane 2,4-Dimethylhexane 2,5-Dimethylhexane 3,4-Dimethylhexane =2,2,3-Trimethylpentane + 2,3,3-Trimethylpentane	− 2900	+ 7.1	− 961	− 783	− 251	+ 459	+ 1169

Table 1.—(*Concluded*)

	Reactions	Free Energy Equations $\Delta F^\circ = A + BT$		ΔF° cal./mol.				
		A	*B*	0°	25°	100°	200°	300°
42	2-Methyl-3-ethylpentane 2,3-Dimethylhexane 2,4-Dimethylhexane 2,5-Dimethylhexane 3,4-Dimethylhexane =2,2,4-Trimethylpentane	− 2900	+ 4.8	− 1589	− 1469	− 1109	− 629	− 149
43	2-Methyl-3-ethylpentane 2,3-Dimethylhexane 2,4-Dimethylhexane 2,5-Dimethylhexane 3,4-Dimethylhexane =2,2,3,3-Tetramethylbutane	− 5800	+14.2	− 1922	− 1567	− 502	+ 918	+ 2338
44	2,3,4-Trimethylpentane =2,2,3-Trimethylpentane =2,3,3-Trimethylpentane	− 1100	+ 3.1	− 253	− 176	+ 57	+ 367	+ 677
45	2,3,4-Trimethylpentane =2,2,4-Trimethylpentane	− 1100	+ 0.8	− 882	− 862	− 802	− 722	− 642
46	2,3,4-Trimethylpentane =2,2,3,3-Tetramethylbutane	− 4000	+10.2	− 1214	− 959	− 194	+ 826	+ 1846
47	2,2,3-Trimethylpentane 2,3,3-Trimethylpentane =2,2,4-Trmethylpentane	0	− 2.3	− 628	− 686	− 858	− 1088	− 1318
48	2,2,3-Trimethylpentane 2,3,3-Trimethylpentane =2,2,3,3-Tetramethylbutane	− 2900	+ 7.1	− 961	− 783	− 251	+ 459	+ 1169
49	2,2,4-Trimethylpentane =2,2,3,3-Tetramethylbutane	− 2900	+ 9.4	− 333	− 98	+ 607	+ 1547	+ 2487
50	Isobutene+Isobutane=2,2,4-Trimethylpentane (isooctane) $\Delta F^\circ = -21965 + 5.435T\log T - 0.25\times10^2T^2 + 24.4T$			−11871	−10906	− 7994	− 4103	− 211

Table 2. Comparison of the $\Delta F°$'s for Isomerization Reaction at 25°C.***

Reactions	$\Delta F°$			
	Wilson*	Hamai	Knowlton[17] Rossini	Pitzer[22]
n-Butane = Isobutane	− 140[11] − 820 (l.)[14b]	− 443 (g.)		− 530 (g.)
Butene-1 = Isobutene	−2540[12]	−2396 (g.)		−2370 (g.)
Butene-1 = Cis-butene-2	−1920[13]	−1234 (g.)		−1240 (g.)
Butene-1 = Trans-butene-2	−2330[14]	−2006 (g.)		−2010 (g.)
Cis-butene-2 = Trans-butene-2	− 410[15]	− 771 (g.)		− 770 (g.)
Cis-butene-2 = Isobutene	− 620[16]	−1161 (g.)		−1130 (g.)
Trans-butene = Isobutene		− 390 (g.)		− 360 (g.)
n-Pentane = 2-Methylbutane (isopentane)	− 100 (l.)[20] −1020 (l.)[19b]	−1097 (g.)	−1095 (g.)** ($\Delta E = -1930 \pm 260$)	−1570 (g.)
n-Pentane = 2,2-Dimethyl-propane (Tetramethyl-methane) (Neopentane)	+ 270 (g.)[20]	−1720 (g.)	−1728 (g.)** ($\Delta E = -4680 \pm 310$)	−1690 (g.)
2-Methyl-butane = 2,2-Dimethyl-propane (isopentane)		− 623 (g.)	− 633 (g.)** ($\Delta E = -2750 \pm 270$)	− 120 (g.)

* E. Wilson, *Chem. Rev.*, **21**(1937), 129–167.

** Calculated by the present author from ΔE's of Rossini.

*** Those data for the unsaturated compounds are from our report II to be published immediately after I.

(11) Arbutzov, *Ber.*, **67**B(1934), 563, 569.

(12) Aschân, *Ann.*, **324**(1902), 12.

(13) Aston and Messerly, *J. Am. Chem. Soc.*, **58**(1936), 2354.

(14) Austorweil, *Bull. soc., chim.*, (4) **39**(1926), 695.

(15) Barrett and Linstead, *J. Chem. Soc.*, (1936), 611.

(16) Berthelot, *Ann. chim. phys.* (7) **20**(1900), 27.

(17) F. D. Rossini and E. J. R. Prosen, *J. Am. Chem. Soc.*, **62**(1940), 2250.

(18) (a) G. S. Parks, Theo. J. West and G. E. Moore, *J. Am. Chem. Soc.*, **63** (1941), 1133–1135.

(b) G. S. Parks, *Chem. Rev.*, **27**(1940), 75–83.

(19) J. W. Knowlton and F. D. Rossini, *J. Res. Natl. Bur. Stand.*, **22**(1939), 415–424.

(20) Rossini, F. D., *J. Chem. Phys.*, **3**(1935), 438.

Table 2.—(*Concluded*)

Reactions	ΔF°			
	Wilson*	Hamai	Knowlton[17] Rossini	Pitzer[21]
n-Hexane = 2-Methylpentane		− 558 (g.)	−1061+230 (g.)	−1080 (g.)
n-Hexane = 3-Methylpentane		− 558 (g.)	− 352+230 (g.)	
n-Hexane = 2,3-Dimethylbutane		−1165 (g.)	− 796+230 (g.)	
n-Hexane = 2,2-Dimethylbutane		−1341 (g.)	−2385+230 (g.)	−2380 (g.)
Hexene-1 = Cyclohexane	−8100			
Hexene-1 = Methylcyclopentane	−12200			
Cyclohexane = Methylcyclopentane	−4100			
	+1150 (l.)[21]			+ 970 (l.)[19b]
n-Heptane = 2-Methylhexane	−1520 (l.)	−1035 (g.)		−1150 (g.)
n-Heptane = 3-Methylhexane	−1120 (l.)	−1035 (g.)		
n-Heptane = 3-Ethylpentane	− 320 (l.)	−1035 (g.)		
n-Heptane = 2,2-Dimethylpentane	− 320 (l.)	−1818 (g.)		−2050 (g.)
n-Heptane = 2,3-Dimethylpentane	− 620 (l.)	−1643 (g.)		
n-Heptane = 2,4-Dimethylpentane	+ 180 (l.)	−1643 (g.)		
n-Heptane = 3,3-Dimethylpentane	+ 920 (l.)	−1818 (g.)		
n-Heptane = 2,2,3-Trimethylbutane	+ 680 (l.)	−2426 (g.)		
Heptene-1 = Methylcyclohexane	−15450 (l.)			
Heptene-1 = 1,2-Dimethyl cyclopentane	−18050 (l.)			
n-Octane = 2,2,4-Trimethylpentane	+ 80 (l.)			
	+2230 (l.)**	−2654 (g.)		−2700 (g.)
n-decane = 2-Methyl-nonane			−1490+670 (l.)[18]	
n-Decane = 5-Methylnonane			−1300+600 (l.)[18]	

(21) A. L. Glasebrook and W. G. Lovell, *J. Am. Chem. Soc.*, **61** (1939), 1717.
(22) K. S. Pitzer, *Chem. Rev.*, **27** (1940), 39–57.
(**) Based on the old data of *n*-octane (E. Wilson).

Table 3. Comparison of Thermodynamic Constants for the Formation of Gaseous Hydrocarbons.

at 298.1 °K (n C (graphite) + m H_2 (g.) = C_nH_{2m} (g.))

Substances	ΔS (Pitzer) cal/deg.	ΔH (Pitzer) K.cal.	$\Delta F°$ K.cal. Pitzer	$\Delta F°$ K.cal. Thacker and Others	$\Delta F°$ K.cal. Egloff	$\Delta F°$ K.cal. Wilson
Methane	− 19.39	−17.865±0.074	−12.085	−12.134	−12.300 (−12.340)	
Ethane	− 41.61	−20.191±0.108	− 7.787	− 7.784	− 8.260 (− 8.730)	
Propane	− 64.4	−24.750±0.124	− 5.55	− 5.576	− 6.220 (− 7.380)	
n-Butane	− 87.5	−29.715±0.153	− 3.63	− 3.748	− 5.000 (− 6.450)	−4.580 (g.) −5.000 (g.) new data
Isobutane	− 91.2	−31.350±0.132	− 4.16	− 4.190	− 4.900 (− 6.850)	−4.720 (g.) −4.900 (g.) new data
n-Pentane	−111.1	−34.739±0.213	− 1.62	− 1.617	− 2.570	−2.570 (g.) −2.820 (l.) −8.600 (l.) old data
2-Methylbutane	−112.3	−36.671±0.153	− 3.19			−2.920 (l.)
Tetramethylmethane	−121.1	−39.410±0.227	− 3.31	− 3.337	− 4.500 (− 6.670)	
n-Hexane	−134.5	−40.01 ±0.50	+ 0.08	− 0.392	− 1.500	−7.000 (l.)
2-Methylpentane	−136.8	−41.8 ±0.7	− 1.0	− 0.950		
2,2-Dimethylbutane	−141.2	−44.4 ±0.7	− 2.3	− 1.733		
n-Heptane	−158.0	−45.35 ±0.80	+ 1.75	+ 1.482	+ 0.190	−1.480 (l.), (new data) −3.000 (l.)
2-Methylhexane	−160.1	−47.1 ±1.00	+ 0.6	+ 0.447	− 1.300	−3.000 (l.)
2,2-Dimethylpentane	−166.2	−49.8 ±1.0	− 0.3	− 0.337	− 0.130	−1.800 (l.)
n-Octane	+181.5	−50.70 ±1.0	+ 3.4	+ 2.518	+ 1.520	−0.850 (l.) (−3.000) +1.520 (g.)
2,2,4-Trimethylpentane	−190.8	−56.2 ±2.0	+ 0.7	− 0.136	+ 1.570	−0.770 (l.)
n-(C_nH_{2n+2}) ($n > 6$)	− 23.49 n +6.4	−(5.35 n−7.90) ±0.12 n	(+1.65 n −9.80)			
Ethylene	− 12.49	+12.556±0.067	+16.279	+16.339	+15.820 (15.530)*	
Propylene	− 32.8	+ 4.956±0.110	+14.73	+14.820	+14.820 (13.920)	
1-Butene	− 55.1	+ 0.383±0.181	+16.81	+17.041	+16.780 (15.330)	
Cis-2-butene	− 56.9	− 1.388±0.181	+15.57	+15.806	+14.860 (14.170)	
Trans-2-butene	− 57.5	− 2.338±0.181	+14.80	+15.035	+14.450 (13.400)	
Isobutene (2-Methyl-propene)	− 59.2	− 3.205±0.162	+14.44	+14.645	+14.240 (13.020)	
Acetylene	+ 14.07	+54.228±0.233	+50.034		+50.840 (49.600)	

(*) Spectroscopic data, assuming free rotation of the C—C bonds (Egloff).

Conclusion. Thus far we have derived the free energy equations of isomerization reactions of the saturated hydrocarbons as a function of temperature and calculated $\Delta F°$'s at various temperatures. They serve to indicate to some extent the general trend of the $\Delta F°$'s values with structural changes. Some correlation and discussion with the so-called "Bond Free Energy Equation" are presented with certain restrictions. Those calculated free energy values for the isomerization from our simple derived equations have been found to give satisfactory results as compared with those given by various authors as K. S. Pitzer, F. D. Rossini, as well as E. Wilson, and some experimental evidences.

Parks and Huffman[23], in 1932, were led to the conclusion that any branched isomer should be on a higher free energy level than the normal compound; while Knowlton and Rossini's data[19][20] have given that just the reverse is true. The situation stimulated such investigators as Montgomery, McAteer and Franke[24] and others to study the isomerization reactions and all these results led to the conclusion supported by Rossini. Our calculations also support that such conclusion is more reasonable.

In conclusion, the author expresses his hearty thanks to Dr. T. Marusawa, Former Director, and to Dr. S. Sato, Director of the Institute, for their interests and constant encouragement in carrying out this investigation and for the permission for this publication. Also the author takes this occasion, to extend his thanks to Dr. R. Negishi who had been willing to participate in discussions as the opportunity demanded in the preparation of this paper.

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(23) Parks and Huffman, "The Free Energies of Some Organic Compounds," 69–72; G. S. Parks, *Chem. Rev.*, **27**(1940), 75–83.

(24) Montgomery, McAteer and Franke, *J. Am. Chem. Soc.*, **59**(1937), 1768.

Über die Beziehung zwischen Herstellungsbedingung und Beständigkeit von Chlorammoniumrauch. (II. Mitteilung der kolloidwissenschaftlichen Untersuchung disperser Systeme, die die Gas-Phase als ein Komponent enthalten).

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(Eingegangen am 17. August 1943.)

(1) *Einleitung*: Da die Entstehungsreaktion formelmässig sehr einfach und die Versuchsmaterialien leicht erhältlich sind, so ist eine ganze Reihe aerokolloidaler Untersuchungen über Chlorammoniumrauch angestellt worden[1]. Physikochemisch ist aber sein Reaktionsmechanismus: $NH_3+HCl=NH_4Cl$ nicht so einfach. Besonders über den Einfluss von Wasserspuren stimmen die theoretischen Meinungen, sowie die experimentellen Ergebnisse verschiedener Autoren noch nicht vollkommen überein[2].

Die aerokolloidale Untersuchung desselben stösst auch in diesem Punkt auf mannigfaltige Schwierigkeiten, welche die Experimente stören und die Zusammenstellung der Versuchsresultate komplizieren. Weil aber sonst keine geeigneten Versuchsmaterialien zu finden sind, haben wir doch an Chlorammoniumrauch systematische kolloidwissenschaftliche Untersuchungen angestellt, unter besonderer Berücksichtigung, um beiliegende chemische Komplikationen möglichst zu vermeiden.

(2) *Versuchsanordnung.* Physikochemisches Feuchtigkeitsproblem möchten wir vorläufig beiseite lassen. Wir bedienten uns nämlich zum Trocknen nicht des gründlichen Verfahrens, wie Vakuum-Fraktionierung unter Anwendung flüssiger Luft, oder langtägiges Trocknen mit P_2O_5[3] usw., sondern benutzten nur gewöhnliche Trocknungsmittel, wie H_2SO_4 und Natronkalk. Das Hauptziel wird zunächst darauf verwendet, die Entstehungsbedingung des Chlorammoniumrauches in Abhängigkeit mit seiner Beständigkeit zu untersuchen. Versuchsmaterialien und ihre Vorbehandlungen sind folgende:

NH_3: Hergestellt durch Erwärmen käuflicher 30% Ammoniak-Lösung. Die Feuchtigkeit wurde entfernt durch Abkühlen mit Eis und Durchleiten durch zwei Natronkalk-Türme.

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(1) R. Tolman, *J. Am. Chem. Soc.*, **41**(1919), 297, 575, 579: R. Whytlaw-Gray, „Smoke", London (1932); A. Winkel und G. Jander, „Schwebestoff in Gasen", Stuttgart (1934); K. Urasowski und R. Kusmenko, *Trans. Fraday Soc.*, **32**(1936), 1054; *J. Phys. Chem.* (U.R.S.S.), **6**(1935), 896; A. Kobayasi und D. Nukiyama, *Proc. phys.-math. Soc. Japan., Ser.* **3**, **14**(1932), 168; **15**(1933), 59.

(2) M. Bodenstein, *Z. physik, Chem.* Abt. B. **20**(1933), 451.

(3) K. Baker, *J. Chem. Soc.*, **65**(1894), 615; **74**(1898), 422: A. Tramm., *Z. physik. Chem.*, **105**(1923), 356: L. Moser „Reindarstellung von Gasen", Stuttgart (1920).

HCl: Hergestellt durch Eintropfen konzentrierter Salzsäure in konzentrierter Schwefelsäure und getrocknet mittels Durchleiten durch zwei Schwefelsäure gefüllte Waschflaschen.

Die Aerosolbildung wurde dadurch gestattet, dass man diese beide Komponentengase aus den Glasdüsen in den Reaktionsraum unter verschiedenen Bedingungen eingeführt hat. Die Beständigkeit des Rauches wurde mit der Durchlässigkeit eines Lichts konstanter Stärke verglichen. Namentlich ist sie ausgedrückt mit der Zeitdauer, dass eine 30 Watt-Glühlampe, die hinter dem Reaktionsraum in bestimmter Entfernung aufgestellt wurde, gerade unsichtbar bleibt. Das Volum des Reaktionsraums ist 1300 cc, dessen Durchmesser und Länge je 8.5 cm und 29 cm beträgt. Zu einem Versuch wurden je 14 cc Komponentengase benutzt.

Der Hauptteil der Apparatur ist schematisch in Abb. 1. skizziert.

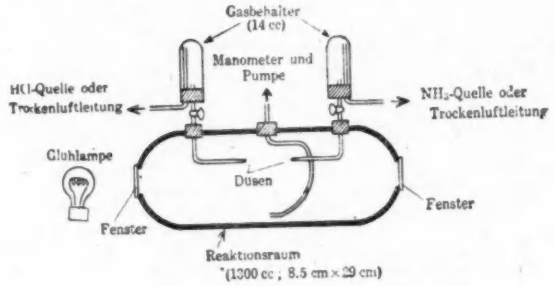

Abb. 1.

(3) *Versuchsergebnisse.* I-Versuch: Versuch mit sehr grossen Düsen. Um die Aerosol-Entstehung möglichst rasch und die Rührung gebildeten Aerosols möglichst vollständig zu machen, so dass man die komplizierte Nebenerscheinung zu beseitigen hoffte, haben wir anfangs die Düsen mit grosser Öffnung (4 mm) benutzt.

Also leitet man zuerst trockne Luft durch die ganze Apparatur 30 Minuten lang hindurch. Der Gasbehälter wurde dann mit getrocknetem NH_3 und HCl erfüllt und der Reaktionsraum ausgepumpt bis zu einem bestimmten Druck. Die Aerosolbildung wurde dadurch gestattet, dass man Komponentengase im Reaktionsraum gleichzeitig einführte.

Der Druckunterschied zwischen Gasbehälter und Reaktionsraum zieht die Gase im Raum hinein und ergibt gleichzeitig die Rührwirkung. Die Versuchsergebnisse sind in Abb. 2 mit ■ oder □ übertragen. Es wurde dadurch gar keine Regelmässigkeit zwischen Druck und Beständigkeit gefunden. Wahrscheinlich wegen zu grosser Düsenöffnungen ging die Gas-Ausströmung d.h. die Rauchbildung unter nicht immer denselben Bedingungen vor sich, welche somit ganz auseinandergehende Resultate verursacht hat.

Die folgenden Versuche wurden deswegen mit Düsen von sehr kleinen Öffnungen (unter 0.5 mm) durchgeführt. II(a)-Versuch: Die Abhängigkeit des Luftdruckes des Reaktionsraums zur Rauchbildung und seine Beständigkeit. Mit dem Öffnen des Behälterhahns wird der Reaktionsraum

augenblicklich mit weissem Rauch erfüllt. Dass die Rauchbildung in der Mitte des Reaktionsraumes beginnt und sich nach beiden Seiten verbreitet, kann man, ausser dem Falle eines kleinen Druckunterschiedes, d.h. grossen Raumdruck, kaum erkennen. Die Ergebnisse sind auf Kurve 1 in Abb. 2 übertragen.

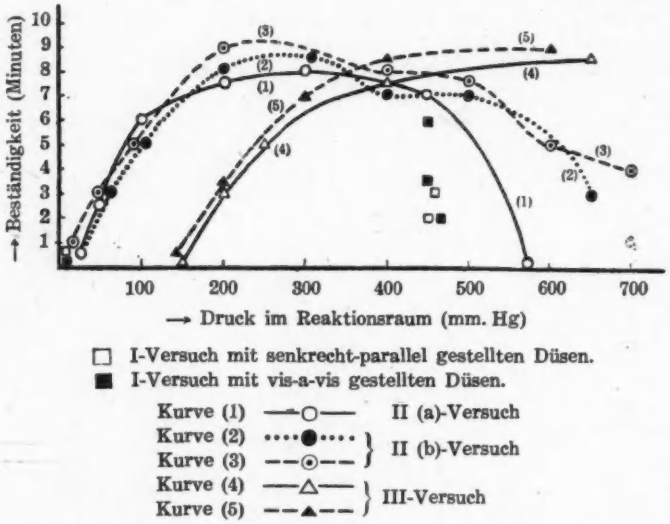

Abb. 2.

Die Abszisse ergibt den Raumdruck vor der Aerosolbildung. Da das Volum des Gasbehälters (14 cc) zu dem des Reaktionsraums (1300 cc) klein ist, so ändert sich der Innendruck des Reaktionsraums vor und nach der Aerosolbildung nur 5–10 mm. Im Raum von sehr kleinem Druck, d.h. fast evakuiertem Raum (unter 5 mm), lässt sich keine Aerosolbildung erkennen. Aber man sieht, dass die Innenwand des Reaktionsraums mit weissem Chlorammonium bedeckt wird. Daraus ist verständlich, dass im Raum mit kleinem Druck die Feuchtigkeit grösstenteils an der Gefässwand adsorbiert, worüber Chlorammonium gebildet war. Mit der Druckzunahme befindet sich die Feuchtigkeit im Reaktionsraum schwebend als Wasserdampf.

Unter dieser Bedingung scheidet Chlorammoniumrauch diesen Wasserdampf als Teilchenkern aus. Es ergibt auch eine Unterstützung, dass Chlorammonium nur im Vorhandensein Spuren von Feuchtigkeit sich entstehen lässt. Bekanntlich kann man die adsorbierte Feuchtigkeit an der Glaswand durch einfaches Durchströmen trockener Luft oder blossem Evakuieren, ohne Erhitzung, nicht entfernen. Die Beständigkeitsabnahme im Gebiet höheren Raumdrucks könnte man durch Zurückbleibens der Komponentengase im Gasbehälter erklären.

Denn in diesem Fall beträgt der Raumdruck 500–600 mm. und nähert sich dem Druck des Gasbehälters (1 Atm., 760 mm), so dass der Druck-

unterschied zwischen ihnen sicher nicht hinreichend ist, um Komponentengase vollständig im Reaktionsraum herauszuziehen. Diese Vermutung wurde mit folgendem II(b)-Versuch bestätigt.

Namentlich haben wir den Gasbehälter, nach dem Erfüllen der Komponentengase, mit einem Quecksilberbehälter verbunden, welcher die Komponentengase mit Quecksilber ersetzend vollständig auszutreiben gestattet. Wie aus den Kurven 2 und 3 in Abb. 2 ersichtlich ist, erhält man mit dieser Einrichtung noch recht beständigen Rauch bis 600–700 mm. Raumdruck.

III-Versuch: Über den Rühreffekt von Luftstrom.

Zum aerokolloidalen System, der Beständigkeit beeinflussender Faktor, rein physikalisch kommt das Rühren in erster Linie in Betracht. Selbstverständlich ist es nötig zum Zweck das System zu homogenisieren. Andererseits darf man aber nicht vergessen, dass ein zu heftiges Rühren im Gegenteil auf die Beständigkeit abnehmend wirkt, weil es den Zusammenstoss der Teilchen, mit anderen Worten, die Koagulation des Aerosols beschleunigt.

Das Verhalten wurde durch den nächsten Versuch geprüft. Die Versuchsanordnung ist wie in II-Versuch. Nur beim Öffnen der Hähne der Gasbehälter öffnet man gleichzeitig die Gaseinfuhrhähne, welche zur Trockenluftleitung gebunden sind. Von den Düsen stürzen also als erstes Moment die Komponentengase — NH_3 und HCl — heraus, wonach strömt die Trockenluft hinein bis Raumdruck zum 1 Atm. egalisiert wird. Dieser Luftstrom, der aus den Düsen in den Reaktionsraum ausgeblasen wird, wirkt ohne weiteres als ein Rührwerk. Die Resultate sind veranschaulicht mit Kurve 4 und 5 in Abb. 2, welche nicht eine Maximumkurve, wie in vorhergehendem Versuch, sondern eine Sättigungskurve darstellt. Unbeständiges Gebiet bei niedrigem Raumdruck steht mit der Vermutung nahe, dass ein zu heftiges Rühren auf die Beständigkeit schädlich wirkt.

(3) *Erörterung.* Es braucht keine besondere Erklärung, dass die Eigenschaften aerokolloidaler Systeme, über haupt die der ganzen kolloiddispersen Systeme, nicht nur von den chemischen Zusammensetzungen disperser Substanzen sowie Dispersionsmittel, sondern von reinen physikalischen Bedingungen bei der Aerosolherstellung stark beeinflusst werden. Bei der Entstehung des Chlorammoniumrauches aus NH_3 und HCl haben wir den einfachsten Fall, die Beeinflussung des Rührens zur Aerosolbeständigkeit untersucht. Zum Rühren wurde nicht ein mechanisches Rührwerk, wie elektrischer Fächer, sondern eine Gasströmung unter Druckunterschied benutzt, die das Rühren im geschlossenen Raum ermöglicht.

Dass ein zu heftiges oder ungenügendes Rühren, gleicherweise der Beständigkeit ungünstig ist, könnte man leicht erwarten, wenn man an eine durch Rühren hervorgerufene Homogenisierung des Systems sowie Zusammenstoss der Teilchen denkt. Aber der merkliche Unterschied der Versuchsergebnisse aus II(a)- und III-Versuch ist beachtenswert. Beim II(a)-Versuch, wo das Rühren nur durch Einströmen eines kleinen Volums der Komponentengase (14 cc) im Reaktionsraum (1300 cc) vor sich geht, erreicht das Beständigkeitsoptimum 160–180 mm Raumdruck. (Siehe Kurve 1 und 2). Hingegen bei III-Versuch, wo das System gründlich mit der Luftströmung umgerührt wird, lässt sich das Beständigkeitsoptimum

erst bei 360–380 mm Raumdruck erkennen. Da die Druckverminderung, die Teilchensedimentierung beschleunigt, muss sie die Beständigkeit negativ beeinflussen[4]. Das Verhalten in Wirklichkeit ist hier umgekehrt, nämlich, im Raum mit vermindertem Druck entsteht mehr beständiger Rauch. Daraus muss man schliessen, dass hier die Beständigkeit nicht von dem absoluten Raumdruck, sondern nur von dem Rühreffekt, welcher durch den Druckunterschied zwischen Reaktionsraum und Gasbehälter hervorgerufen wird, abhängig ist.

Beim II(a) Versuch wurden nur beide Komponentengase — NH_3 und HCl — im Reaktionsraum unter verschiedenem Druck eingeführt, wofür höchstens einige Zehntel von Sekunden hinreichend sind.

Hier endet die Rührung momentan durch Einspritzen beider Gase. In dissem Fall könnte man sagen das Rühren ist, „kurz aber scharf." Warum diese Rührmode bei verhältnismässig niedrigerem Raumdruck das Beständigkeitsmaximum hervorruft, können wir noch nicht sicher beantworten. Vielleicht findet man die Erklärungsmöglichkeit aus der Tatsache, dass das Rühren in diesem Fall mit der Aerosolentstehung schon aufgehört hat, worüber noch eingehende Untersuchungen nötig sind. Die Beständigkeitsherabsetzung höheren Raumdrucks, ist leicht verständlich durch Zurückbleibens der Komponentengase. Die Vermutung wurde, wie erwähnt, in II(b)-Versuch bestätigt durch Gasaustreibung mit Quecksilber. (Siehe Kurve 2 und 3, Abb. 2.)

In III-Versuch, wo das System nach dem Aerosolentstehen weiter zum Druckvergleich des Reaktionsraumes bis zu 1 Atm. mit Lufteinströmen umgerührt wird, wird das Beständigkeitsoptimum erst bei 360–380 mm (Abb. 2, Kurve 4 und 5) erreicht.

Der Ausgangsraumdruck unter 350 mm verursacht vielleicht zu heftiges Rühren, welches wie schon betont, auf die Beständigkeit ungünstig wirkte. Beschliessend kann man sagen, dass ein mehr leises Rühren der Beständigkeit wohl vorteilhafter ist.

Jedenfalls wurde gezeigt, dass eine reine physikalische Bedingung, wie z.B. das Umrühren, zur Entstehung, Beständigkeit und anderen Eigenschaften eines Aerosols von grosser Bedeutung ist. Der Versuch weiterer Möglichkeiten der Variationen der Versuchsbedingungen ist schon im Gang.

Zusammenfassung.

(1) Kolloideigenschaften des Chlorammoniumrauches hauptsächlich in Beziehung seiner physikalischen Entstehungsbedingungen wurden untersucht.

(2) NH_3 und HCl wurden durch die Glasdüsen in den Reaktionsraum, unter verschiedenen Bedingungen, eingeführt, wodurch die Rauchbildung gestattet wird.

(3) Die Düsen mit zu grossen Öffnungen führt zu voneinander ganz unregelmässigen Ergebnissen, wohingegen mit den Düsen geeigneter

(4) *Loc. cit.* „Smoke" S. 62; J. Sameshima, *Kagaku-Sôhô*, No. 3, S. 69, Tokyo (1942).

Öffnungen sich sehr gut Variationen der Entstehungsbedingungen erkennen lassen.

(4) Wenn nur beide Komponentengase im Reaktionsraum verschiedenen Drucks eingeführt wurden, zeigt die Aerosolbeständigkeit eine Optimumbeziehung gegen Raumdruck.

(5) Wenn der Reaktionsraum nach der Aerosolentstehung mit Luftstrom umgerührt wird, ergibt die Beständigkeit und der Ausgangsdruck die Sättigungsbeziehung.

(6) Dieses Verhalten wurde vorläufig aus homogenisierendem und koagulierendem Effekt des Umrührens erklärt, welches von der Gasströmung unter Druckunterschied hervorgerufen wird.

Diese Untersuchung wurde auf Kosten der Ausgaben des Unterrichtsministeriums für wissenschaftliche Forschung ausgeführt.

Chemisches Institut der Kaiserlichen Universität zu Osaka und Siomi-Institut für physikalische und chemische Forschung.

Über die Wirkung von Ultraschall auf Kolloiderscheinungen. IX-Mitteilung[1]: Das Verhalten der Flüssigkeiten im Ultraschallfeld in Abhängigkeit ihrer Viskositäten.

Von Haruhiko OKUYAMA.

(Eingegangen am 31. August 1943.)

(1) Einleitung.

Infolge der kleinen Absorption oder grossen Durchlässigkeit, ist die chemische bzw. kolloidwissenschaftliche Wirkung von Ultraschall meistens in flüssigen Medien bearbeitet worden.[2] Um die flüssige Probe mit Ultraschall zu beschallen, mit Ausnahme ganz spezieller Fälle,[3] wird sie in ein Gefäss im Ultraschallfeld, welches in einem Ölbad entstanden ist, gebracht.

Dann müssen die Schallwellen, welche von einer Quarzplatte oder anderen Oszillatoren ausgegangen sind, bevor sie die Probeflüssigkeiten erreichen durch ein Ölbad unbestimmter Tiefe und durch die Gefässwand von verschiedener Dicke, Form und Material hindurchgehen.

Mit anderen Worten, der Ultraschall muss, bevor er die beschallende Probe erreicht, zuerst zwei andere Substanzen, namentlich Ölbad und Gefässmaterial und zwei Grenzflächen unbestimmter Formen, d.h. Aussen- und Innenwand des Gefässes hindurchgehen.

Dann ist es ohne weiteres verständlich, dass die Absorption, Reflexion, Refraktion, Diffraktion und andere schallphysikalischen Probleme parallel den chemischen sowie kolloidwissenschaftlichen Wirkungseffekten berücksichtigt werden müssen. Da die ganz gleichen Umstände in Probeflüssigkeiten wieder zu berücksichtigen sind, werden die Wirkungsweise und Effekte des Ultraschalls auf flüssigen Proben recht komplizierter Natur, worüber eine gründliche und systematische Untersuchung von neuem erwünscht wird.[4] Der erste Schritt wird mit nachstehendem Versuch unter besonderer Berücksichtigung ihrer Viskositäten unternommen.

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(1) N. Sata, *Kolloid-Z.*, **71**(1935), 48; N. Sata und S. Watanabe, *Kolloid-Z.*, **73**(1935), 50; **78**(1937), 277; **81**(1937), 182; N. Sata und Y. Niwase, *Kolloid-Z.*, **81**(1937), 294; N. Sata und N. Naruse, *Kolloid-Z.*, **86**(1939), 102; **89**(1939), 341; N. Sata, **87**(1939), 185; **88**(1939), 182; N. Sata und Y. Harisaki, dieses Bulletin, **15**(1940), 180; N. Sata und K. Nakasima, dieses Bulletin, **18**(1943), 220.

(2) N. Sata, "Kagaku-Zikkengaku", Bd. IV, S. 290, Tokyo (1942).

(3) S. Morita, *Mazda-Kenkyû-Zihô*, **17**(1942), 308.

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